RENDICONTI SOCIETÀ ITALIANA DI MINERALOGIA E PETROLOGIA, 1986, Vol. 41 (1), pp. 25-39

# Chemical features of wallrocks from Mo-showings of Sardinia (Italy)

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ABSTRACT. — Major and selected trace-element abundances of some samples of Mo-bearing granitoid rocks (mainly leucogranites) from Sardinia have been measured. Several microprobe analyses of sericite, chlorite and biotite and analyses of unmineralized rocks from the same outcrops have also been carried out.

Chemistry of the rocks analyzed shows that the emplacement of the Mo ores was accompanied by weak alteration of the host rocks, that was performed by acidic fluids closely connected as origin with the intrusion of the granitic magmas. Alteration is characterized in most rocks by an increase of $SiO_2$ and a decrease of $Al_2O_3$, all other major elements exhibiting no characteristic variations. $TiO_2$, MnO and $P_2O_5$ exhibit lower contents in most rocks with respect to unaltered rocks of similar $SiO_2$ content. Finally, among trace elements, only Ba and to lower extent also Sr, decrease with increasing $SiO_2$, all other trace elements displaying rather constant abundances in most rocks.

*Key words*: molybdenum, alteration, granitoid rocks, ores, Sardinia.

RIASSUNTO. — Sono state misurate le abbondanze degli elementi maggiori e di selezionati elementi traccia in alcuni campioni di rocce granitoidi della Sardegna contenenti mineralizzazioni a molibdenite. Sono state inoltre effettuate analisi di campioni di rocce non mineralizzate degli stessi depositi ed analisi alla microsonda elettronica di minerali quali clorite, sericite e biotite.

La composizione chimica delle rocce analizzate mostra che la formazione delle mineralizzazioni fu accompagnata da debole alterazione delle rocce ad opera di fluidi acidi, la cui origine è strettamente connessa con l'intrusione dei magmi granitici. L'alterazione è caratterizzata nella maggioranza delle rocce da un aumento della silice e una diminuzione dell'allumina; tutti gli altri ossidi maggiori non presentano variazioni di contenuto importanti. $TiO_2$, MnO e $P_2O_5$ mostrano in genere contenuti più bassi nella maggioranza delle rocce rispetto a rocce inalterate di corrispondente valore della silice. Infine, tra gli elementi traccia solamente il bario, ed in certa misura anche lo stronzio, decrescono come contenuto nelle rocce all'aumentare della silice, mentre tutti gli altri mostrano abbondanze abbastanza costanti nella maggioranza delle rocce analizzate.

*Parole chiave*: molibdeno, alterazione, granitoidi, mineralizzazioni, Sardegna.

## Introduction

Mo showings in Sardinia are known since least century (JERVIS, 1873; LOVISATO, 1886; TRAVERSO, 1898), but only recently they have raised new interest (e.g. SALVADORI, 1959; BACCOS, 1968; HALL, 1975; GHEZZO et al., 1981; GUASPARRI et al., 1981, 1984; BRALIA et al., 1983 a, b). In fact, although they have no economic value, the bulk of molybdenum being distributed through large rock volumes, their study may be useful not only for explaining their genesis, but also for prospecting.

In this view we have analyzed the wallrocks of several major Mo showings of Sardinia with respect to major and selected trace elements.

We have considered the Sardinian Mo showing as a whole mineralization, as they show many close features and, moreover, are genetically related to the same magmatic cycle.

## The materials studied

The Sardinian Mo showings, the locations of which are reported in fig. 1, occur within granitoid rocks that are fine-grained leucogranites and porphyritic leucogranites, except for showings from Ogliastra that are related to granodiorites. All these igneous rocks belong to the Sardo-Corsica batholith of Hercynian age. In particular the leucogranites were emplaced during the last stage of the Hercynian magmatic cycle, while the granodiorites represent products of earlier stages (BRALIA et al., 1982). According to GUASPARRI et al. (1984) there is a genetic link between the hypoabyssal rocks of the leucogranitic suite and the Mo showings. This link exists also in the case of the showings from Ogliastra, as, despite their occurrence within the granodiorites, they would be connected with hydrothermal circulation related to the intrusion of a system of great leucogranite-porphyry dikes.

The Sardinian Mo showings occur as stockworks, quartz veins, fracture fillings and disseminations in the granitoid rocks. There is a close relationship between ore occurrence and paragenesis; in particular disseminated-Mo ores are associated with sphalerite, chalcopyrite, wolframite and pyrite, while $MoS_2$ from the other occurrences is associated with galena, sphalerite and pyrite. According to GHEZZO et al. (1981) hydrothermal halos with propylitic, argillic and phyllic assemblages are associated with the showings, that have thus been referred as porphyry-style mineralization. However, only in a few occurrences as at Perda Lada, hydrothermal halos of different mineral assemblages are arranged in roughly concentric zones, suggesting patterns of typical porphyry-ore deposits.

Hydrothermal alteration scarcely penetrates into the metamorphic cover, affecting preferentially the igneous rocks. According to GUASPARRI et al. (1984) alteration of higher degree is mainly associated with disseminated-Mo ores.

A brief description of the main characteristics of the Sardinian Mo showings studied is given in the appendix. Geological information on the Sardinian granitoids and related Mo showings is reported by BRALIA et al. (1982) and GUASPARRI et al. (1984), respectively.

The rocks studied in this paper were collected from Mo showings moving away from the mineralized spots towards the unmineralized rocks. With respect to the type of $MoS_2$ occurrence in the mineralized rocks, this sulfide may occur disseminated or host in quartz-bearing veinlets (stockworks). These two types of occurrence are sometimes associated in a same showing. $MoS_2$ may also fill in some little fractures of the rocks, but this third occurrence type is of very subordinate importance. The unmineralized (barren) rocks, generally showing no evident

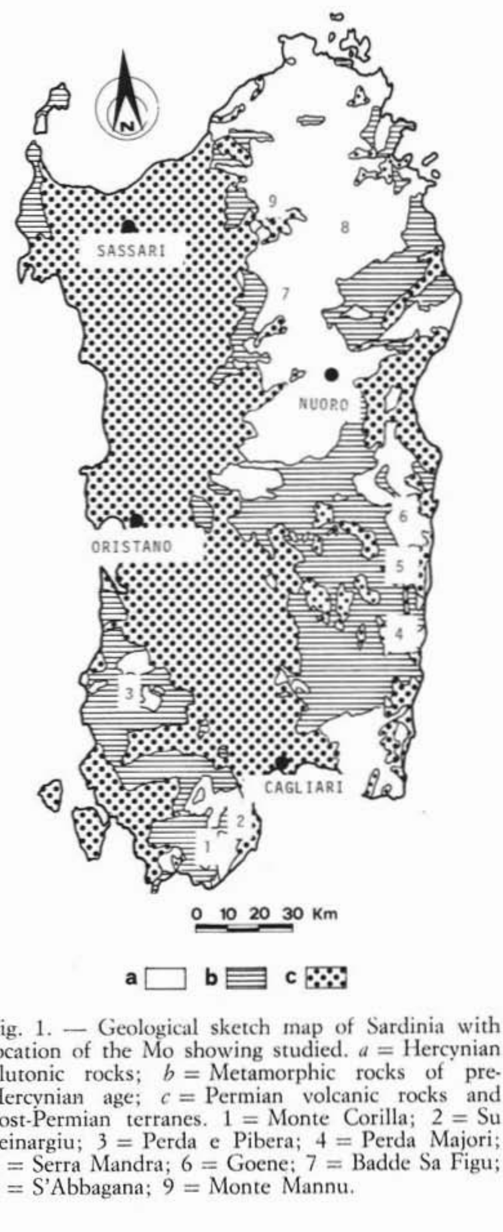



Fig. 1. — Geological sketch map of Sardinia with location of the Mo showing studied. $a$ = Hercynian plutonic rocks; $b$ = Metamorphic rocks of pre-Hercynian age; $c$ = Permian volcanic rocks and post-Permian terranes. 1 = Monte Corilla; 2 = Su Seinargiu; 3 = Perda e Pibera; 4 = Perda Majori; 5 = Serra Mandra; 6 = Goene; 7 = Badde Sa Figu; 8 = S'Abbagana; 9 = Monte Mannu.

alteration were often collected at very short (from a ten to a hundered meters depending on the type of occurrence and size of the mineralization) distance from the mineralized rock.

Most of the mineralized rocks studied show alteration of primary mineral phases such as biotite to chlorite and of plagioclase, only occasionally also of K-feldspar and biotite, to sericite. This latter, however, is always formed in small amount, thus suggesting a moderately low grade of alteration. Secondary quartz often fills in the fractures of the rocks and pyrite occurs as disseminated starlets.

Of subordinate importance is another type of alteration that is characterized by the association of chlorite, carbonate and clay minerals, chlorite and clay minerals substituting in particular for biotite and plagioclase, respectively. Epidote may occur in this assemblage, but it is generally rare in all outcrops studied, except in those from Ogliastra. Late calcite sometimes occurs in little veins crosscutting the altered rocks. Due to the low abundance of calcite and epidote it is questionable if this assemblage can be referred as propylitic.

## Analytical procedure

All rocks have been studied for major and trace elements, except Li and F, by means of XRF analysis, following the procedure of FRANZINI et al. (1972) for major and minor elements, and LEONI and SAITTA (1976) for trace elements, respectively. Li has been determined by flame spectrophotometry and F with a sensitive electrode technique. The precision and accuracy of measurements have been calculated against several international standards, and they were better than 10 % for trace elements.

## Results and discussion

Major and selected trace-element abundances of the granitoid rocks from the Sardinian Mo showings studied are give in tab. 1. These data are plotted versus $SiO_2$ in fig. 2 and fig. 3, as the content of this oxide increases in most rocks with the respect to the Sardinian unaltered granitoids.

Tab. 2 shows the chemical analyses of selected mineral phases from three major Mo showings. Finally fig. 4 compares the averages of major, selected trace elements and some element ratios in both the barren and mineralized rocks. Since there is a great difference of chemistry and mineralogy between leucogranites and Ogliastra biotite granodiorites, the analytical data are presented and discussed separately for the two rock-types, dealing first with the more numerous leucogranitic rocks.

From fig. 2 it is apparent that among major elements $Al_2O_3$ is the only oxide that decreases systematically with increasing $SiO_2$ in most rocks, as generally observed in silicification processes. However it shows no significant variation in most disseminated-$MoS_2$ bearing rocks with respect to averages of unaltered leucogranites from Sardinia (BISTE, 1982; GUASPARRI et al., 1984), indicating scarce, or even null, alteration of aluminosilicates in these rocks.

Relative to averages of unaltered leucogranites MgO and $Fe_2O_{3\,tot}$ stay constant in many rocks. As Mg and Fe are mainly borne by biotite in the unaltered rocks, it is apparent that alteration of this phase to chlorite caused only minor variations of content of both elements, in agreement with the data of tab. 2 showing chlorite contains similar Mg and higher Fe contents than biotite in the rocks studied. From the same data it is also seen that alteration of biotite to sericite, that as said above is of subordinate importance, may account for the low Fe contents of some barren rocks, but it does not explain why these latter exhibit no paralle depletion in MgO as to be expected because of the very low Mg contents of sericite. This discrepancy has no ready explanation. Finally, sample Mo-16 shows the highest MgO and $Fe_2O_{3\,tot}$ contents of all samples analyzed, suggesting the presence of a relatively abundant Fe-oxide phase in this rock.

$K_2O$ is constant in most rocks with respect to averages of Sardinian unaltered leucogranites, showing however a depletion and, conversely, an increase in some mineralized and barren rocks, respectively. As suggested from tab. 2 data, enrichment in K may be explained by alteration of plagioclase to sericite, while depletion is likely due to alteration of K-bearing phases, particularly chloritization of biotite.

TABLE 1
*Major (wt %) and selected trace-elements (ppm) contents in the wallrocks from the Sardinian Mo showings*

| locality | SU SEINARGIU | | | MONTE CORILLA | | | | PERDA E PIBERA | |
|---|---|---|---|---|---|---|---|---|---|
| sample | $Mo_1$ | $Mo_2$ | $Mo_3$ | $Mo_4$ | $Mo_5$ | $Mo_6$ | $Mo_7$ | $Mo_8$ | $Mo_9$ |
| $SiO_2$ | 77.75 | 82.81 | 75.94 | 80.10 | 78.93 | 77.16 | 77.80 | 79.85 | 79.74 |
| $Al_2O_3$ | 11.84 | 9.48 | 12.57 | 10.05 | 11.28 | 10.24 | 11.83 | 10.00 | 9.86 |
| $Fe_2O_3$ * | .74 | .46 | .95 | 1.02 | .30 | .34 | .27 | 1.44 | 1.21 |
| CaO | .30 | .09 | .59 | .03 | .07 | 2.60 | .14 | .55 | 1.13 |
| MgO | .21 | .19 | .21 | .22 | .25 | .06 | .22 | .17 | .35 |
| $Na_2O$ | 3.37 | 3.64 | 3.90 | .87 | 1.82 | 2.61 | 2.87 | 2.69 | 2.48 |
| $K_2O$ | 4.87 | 2.57 | 4.98 | 6.95 | 6.66 | 5.32 | 6.31 | 4.29 | 4.06 |
| MnO | .01 | .01 | .02 | ND | ND | ND | ND | .02 | .04 |
| $P_2O_5$ | .02 | .02 | .03 | .02 | .03 | .03 | .02 | .02 | .02 |
| $TiO_2$ | .07 | .06 | .07 | .03 | .04 | .05 | .05 | .07 | .05 |
| L.O.I. | .82 | .67 | .77 | .71 | .62 | 1.59 | .49 | .90 | 1.06 |
| Zn | 13 | 10 | 16 | 28 | 18 | 25 | 20 | 25 | 23 |
| Cu | 10 | 9 | 10 | 13 | 12 | 13 | 15 | 13 | 12 |
| Ce | 46 | 25 | 48 | ND | 16 | ND | 26 | 28 | 33 |
| Ba | 102 | 72 | 96 | 224 | 63 | 32 | 38 | 85 | 52 |
| La | 12 | 14 | 15 | ND | 7 | ND | 14 | 12 | 15 |
| Zr | 86 | 72 | 79 | 57 | 81 | 62 | 73 | 79 | 69 |
| Sr | 27 | 27 | 26 | 16 | 10 | 12 | 13 | 25 | 19 |
| Rb | 247 | 156 | 275 | 226 | 250 | 189 | 260 | 250 | 266 |
| Pb | 25 | 3 | 29 | 27 | 31 | 30 | 34 | 34 | 32 |
| Li | 6 | 13 | 8 | 8 | 4 | 4 | 3 | 19 | 9 |
| F | 402 | 427 | 448 | ND | ND | ND | ND | 583 | 4000 |
| Symbol | ● | × | ● | × | ● | ● | ● | ● | × |

* TOTAL IRON AS $Fe_2O_3$

*Symbols*: ▲ = disseminated-$MoS_2$ bearing rocks; × = rocks bearing $MoS_2$ in quartz veins; ● = barren rocks.

CaO does not vary significantly in most rocks relative to averages of unaltered leucogranites, being somewhat lower only in a few rocks likely because of plagioclase alteration. CaO shows the highest value in sample Mo-6, that is affected by carbonate alteration.

To alteration of plagioclase are also referred the lower contents of $Na_2O$ of most barren rocks with respect to average unaltered Sardinian leuçogranite. Mineralized rocks show large scatter, with the average close to that of unaltered rocks. This suggests only slight alteration of plagioclase in these rocks.

$P_2O_5$ is low in most rocks with respect to averages of unaltered leucogranites and does not show any correlation with

TABLE 1 (*continued*)

| locality | PERDA MAJORI | | | | MONTE MANNU | | | | BADDE SA FIGU |
|---|---|---|---|---|---|---|---|---|---|
| sample | $Mo_{12}$ | $Mo_{13}$ | $Mo_{14}$ | $Mo_{15}$ | $Mo_{16}$ | $Mo_{17}$ | $Mo_{18}$ | $Mo_{19}$ | $Mo_{20}$ |
| $SiO_2$ | 76.55 | 77.90 | 76.09 | 77.11 | 76.93 | 76.37 | 75.05 | 75.26 | 79.46 |
| $Al_2O_3$ | 11.28 | 11.08 | 12.56 | 12.03 | 10.26 | 12.57 | 12.67 | 12.74 | 10.75 |
| $F_2O_3$ * | 1.63 | 1.06 | 1.34 | 1.03 | 3.89 | 1.06 | 1.33 | .92 | 1.39 |
| CaO | .29 | .26 | .30 | .23 | .86 | 1.17 | .88 | .97 | .70 |
| MgO | .24 | .21 | .29 | .21 | .87 | .37 | .37 | .28 | .40 |
| $Na_2O$ | 1.25 | 1.92 | 3.60 | 3.74 | 2.73 | 3.15 | 3.34 | 3.64 | 3.16 |
| $K_2O$ | 7.58 | 6.57 | 5.10 | 4.71 | 3.20 | 4.32 | 4.69 | 5.17 | 3.51 |
| MnO | ND | ND | .05 | .05 | .10 | .03 | .02 | .01 | .06 |
| $P_2O_5$ | .14 | .07 | .03 | .02 | .05 | .02 | .02 | .27 | .02 |
| $TiO_2$ | .35 | .31 | .09 | .05 | .23 | .04 | .04 | .11 | .04 |
| L.O.I. | .69 | .85 | .55 | .82 | .87 | .89 | .57 | .64 | .50 |
| Zn | 28 | 33 | 78 | 23 | 19 | 15 | 12 | 10 | 25 |
| Cu | 15 | 19 | 17 | 11 | 11 | 10 | 10 | 11 | 12 |
| Ce | 23 | 16 | 36 | 25 | 77 | 44 | 30 | 13 | 17 |
| Ba | 864 | 737 | 323 | 79 | 345 | 178 | 295 | 169 | 55 |
| La | 13 | 5 | 16 | 12 | 39 | 17 | 15 | ND | 10 |
| Zr | 104 | 80 | 86 | 53 | 135 | 64 | 63 | 39 | 71 |
| Sr | 98 | 62 | 50 | 18 | 46 | 21 | 24 | 78 | 13 |
| Rb | 238 | 234 | 333 | 302 | 183 | 171 | 178 | 216 | 272 |
| Pb | 124 | 30 | 39 | 41 | 12 | 11 | 18 | 30 | 15 |
| Li | 8 | 15 | 87 | 50 | 10 | 8 | 7 | 4 | 17 |
| F | 543 | 563 | 1020 | 594 | 1350 | 448 | ND | 343 | 1228 |
| Symbol | ● | ● | ▲ | x | ▲ | ▲ | ▲ | ● | x |

* TOTAL IRON AS $Fe_2O_3$

increasing $SiO_2$. The low contents of this oxide in the rocks studied are perhaps due to analytical uncertainty. The highest contents of samples Mo-12 and Mo-19 suggest a greater abundance of apatite and/or other phosphate phase in these rocks.

Finally MnO and $TiO_2$ are lower in most rocks than in average unaltered leucogranite. Alteration of biotite to sericite may account for the decrease of both elements as indicated by tab. 2 data showing lower Ti and Mn contents in sericite with respect to the coexisting biotite.

From the same data it is also apparent that, as chlorite is a Ti-poor phase in the rocks studied, chloritization of biotite may decrease Ti content of the rocks. Chloritization of biotite may also bring Mn depletion, as chlorite contains somewhat lower MnO than biotite. However alteration of some other phase (Fe oxides?) may contribute to further decrease Mn levels. A few rocks, such as samples Mo-12, Mo-13 and Mo-16, display higher $TiO_2$ contents than averages of unaltered rocks, likely due to the presence of relatively abundant Fe-oxides in these rocks.

Among trace elements (fig. 3) Li is lower in most rocks, and in particular in the barren ones, relative to average of unaltered leuco-

TABLE 1 *(continued)*

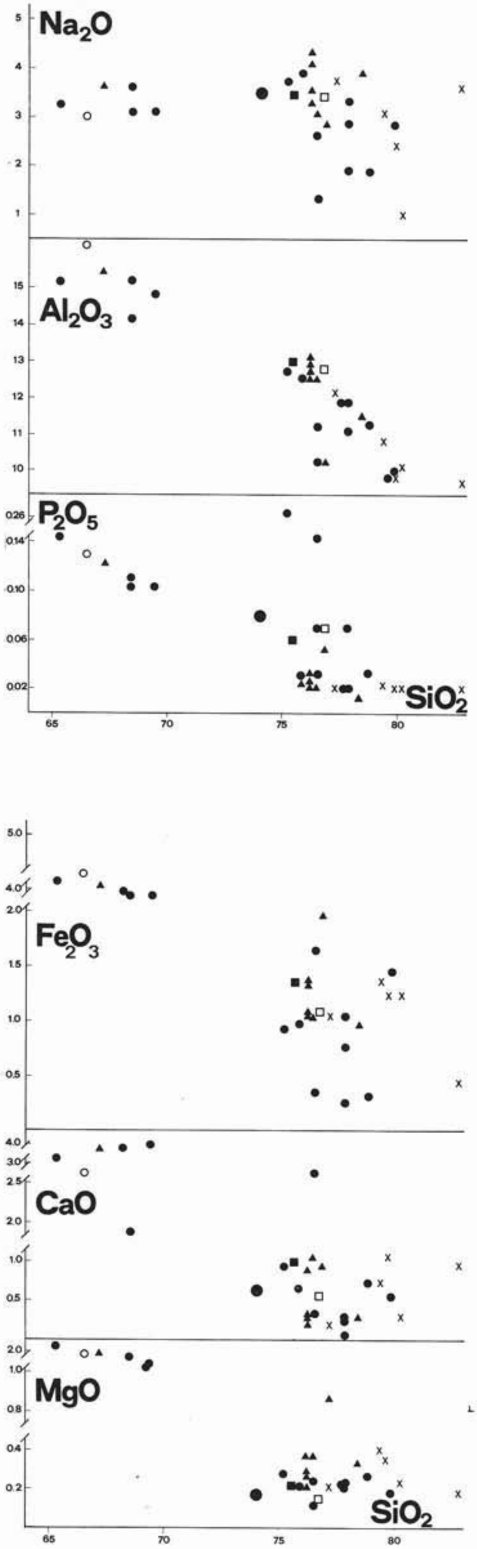
| locality | S'ABBAGANA | | | GOENE | | | SERRA MANDRA | |
|---|---|---|---|---|---|---|---|---|
| sample | $Mo_{21}$ | $Mo_{22}$ | $Mo_{23}$ | $Mo_{24}$ | $Mo_{25}$ | $Mo_{26}$ | $Mo_{27}$ | $Mo_{28}$ |
| $SiO_2$ | 78.35 | 76.07 | 76.02 | 65.21 | 67.11 | 68.44 | 69.23 | 68.38 |
| $Al_2O_3$ | 11.48 | 12.83 | 12.82 | 15.37 | 15.68 | 14.13 | 14.80 | 15.22 |
| $Fe_2O_3$ * | .94 | 1.09 | 1.03 | 5.13 | 4.10 | 3.73 | 3.17 | 3.90 |
| CaO | .32 | .27 | .19 | 3.20 | 3.59 | 1.89 | 3.92 | 3.95 |
| MgO | .34 | .25 | .22 | 2.19 | 1.73 | 1.76 | 1.33 | 1.45 |
| $Na_2O$ | 3.82 | 4.26 | 4.16 | 3.27 | 3.60 | 3.62 | 3.12 | 3.09 |
| $K_2O$ | 4.13 | 4.52 | 4.96 | 3.94 | 3.13 | 4.49 | 2.64 | 2.93 |
| MnO | .03 | .05 | .07 | .10 | .05 | .07 | .05 | .05 |
| $P_2O_5$ | .01 | .02 | .02 | .14 | .12 | .10 | .10 | .11 |
| $TiO_2$ | .03 | .03 | .04 | .70 | .56 | .48 | .42 | .45 |
| L.O.I. | .55 | .60 | .47 | .62 | .31 | 1.03 | .98 | .75 |
| Zn | 27 | 28 | 36 | 76 | 165 | 59 | 41 | 49 |
| Cu | 11 | 11 | 12 | 8 | 93 | 39 | 35 | 34 |
| Ce | 46 | 34 | 40 | 51 | 73 | 89 | 58 | 48 |
| Ba | 23 | 29 | 27 | 563 | 443 | 619 | 482 | 484 |
| La | 11 | 9 | 16 | 21 | 42 | 22 | 18 | 26 |
| Zr | 73 | 69 | 73 | 140 | 139 | 137 | 111 | 125 |
| Sr | 11 | 14 | 13 | 184 | 210 | 177 | 230 | 221 |
| Rb | 462 | 496 | 456 | 172 | 131 | 154 | 106 | 112 |
| Pb | 37 | 33 | 44 | 48 | 30 | 35 | 47 | 31 |
| Li | 22 | 20 | 13 | 43 | 34 | 26 | 44 | 22 |
| F | 685 | 417 | ND | 600 | 370 | 248 | 290 | 96 |
| Symbol | ▲ | ▲ | ▲ | ● | ▲ | ● | ● | ● |

* TOTAL IRON AS $Fe_2O_3$

granites (BISTE, 1982), in agreement with alteration of biotite, that is probably the main Li carrier in the unaltered rocks. Some mineralized rocks from Perda Majori deposit show a relatively strong enrichment, indicating that relatively volatile-rich fluids were involved in the genesis of this showing, in agreement with the presence of topaz in the rock paragenesis.

Rb and Pb generally show no major variations with increasing $SiO_2$ in all rocks, except those containing disseminated-$MoS_2$. These latter, in fact, show both enrichment as at S'Abbagana deposit, and depletion as at Monte Mannu deposit, indicating quite opposite alteration patterns in the rocks from these two showings.

In particular alteration of biotite, that is a main Rb and Pb carrier in the Sardinian unaltered leucogranites, to chlorite may cause Rb impoverishment of the rocks, as chlorite is a Rb (and likely Pb)-poor phase. On the contrary, as suggested by tab. 2 data, sericitization of biotite causes little variation of Rb content in the rocks (and perhaps also of Pb). Moreover sericitization of plagioclase may even concentrate Rb and Pb, as this feldspar is a phase very poor in these elements, thus leading to a potential enrichment of the rocks. Finally, sample Mo-12



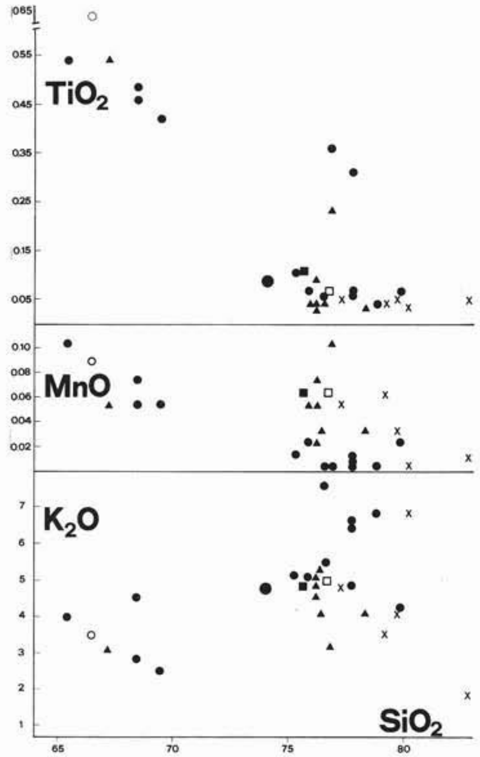
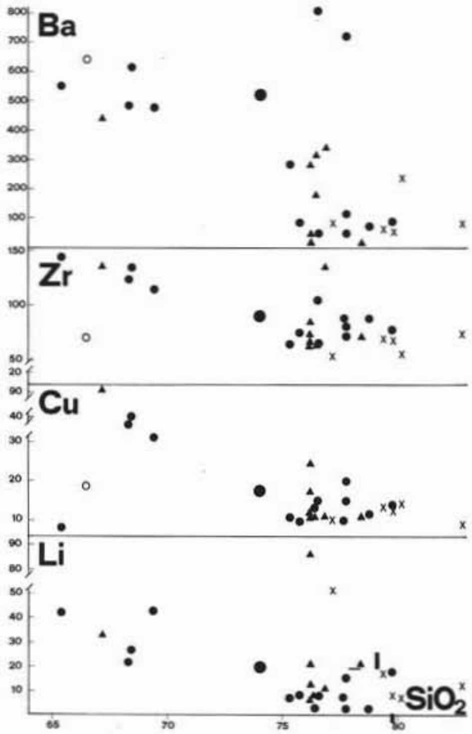



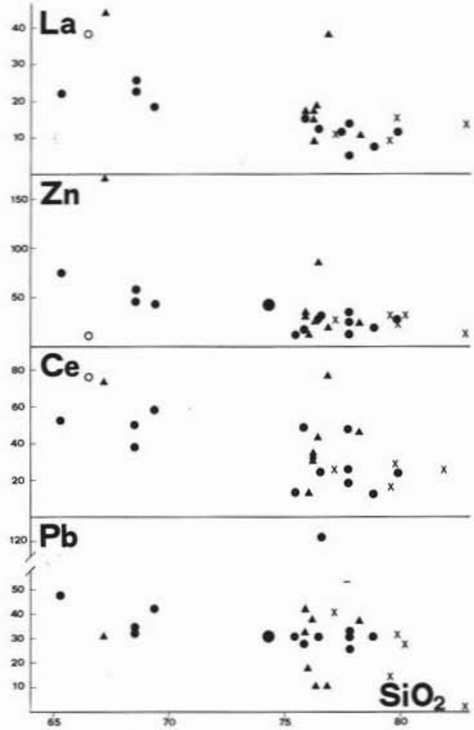

Fig. 2. — Relationship of major oxides versus $SiO_2$ in the wallrocks from the Sardinian Mo showings studied. ● = barren rocks; ▲ = disseminated-$MoS_2$ bearing rocks; × = rocks bearing $MoS_2$ in quartz veins; ○ = « average » granodiorite from Ogliastra (Fiori et al., 1984); big ● = « average » leucogranite from Southern Sardinia (Biste, 1982); ■ and □ = « average » leucogranite and porphyritic leucogranite from Sardinia (Guasparri et al., 1984), respectively.

shows the highest Pb content among all samples studied, likely in relation to the presence of some galena in this rock.

Sr, and much more Ba, are generally depleted in most rocks relative to average unaltered leucogranite, except in samples Mo-12 and Mo-13 that contain a small amount of barite. Depletion of these two elements is clearly referred to alteration of plagioclase (Sr) and K-bearing phases (Ba), mainly biotite.

F shows roughly constant contents in most rocks, only a few of them, and significantly all mineralized, displaying a sensible enrichment. The highest content of sample Mo-9 is accounted for by the presence of fluorite in the rock paragenesis.



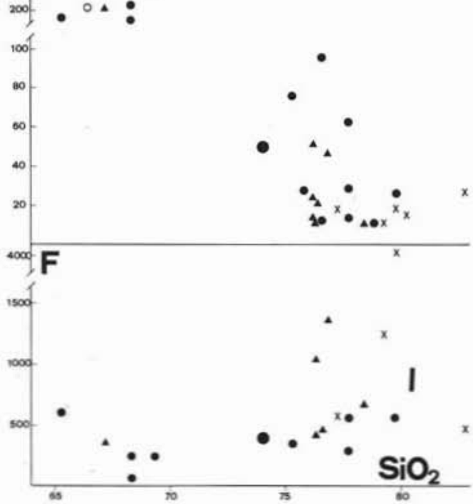




Fig. 3. — Relationship of selected trace elements versus $SiO_2$ in the wallrocks from the Sardinian Mo showings studied. Symbols as in fig. 2.

Zr, Cu and Zn show rather constant contents with increasing $SiO_2$, although perhaps somewhat lower than average of unaltered leucogranites. In particular there is evidence that zircon, as to be expected, was a stable phase during alteration of the rocks studied. Some Cu and Zn were possibly lost during alteration of biotite, that is likely the main carrier of these elements in the unaltered rocks.

No comparison can be done for La and Ce with averages of these elements in Sardinian unaltered leucogranites, as data in this respect lack. However from fig. 3 it is apparent that these elements show no particular trend with increasing $SiO_2$, suggesting that their contents did not vary significantly with alteration in the rocks studied and thus the host phase(s) was stable. Sample Mo-16 shows the highest La and Ce contents among all rocks. As this sample exhibits also the highest Zr content, there is suggestion that

TABLE 2

*Microprobe analyses of selected mineral phases of the wallrocks from three Sardinian Mo showings*

| mineral phase | SERICITE | | | CHLORITE | | |
|---|---|---|---|---|---|---|
| sample | $Mo_{18}$ | $Mo_{15}$ | $Mo_8$ | $Mo_{18}$ | $Mo_{18}$ | $Mo_8$ |
| $SiO_2$ | 46.61 ± 1.38 | 45.05 ± 1.38 | 46.25 ± .99 | 22.38 ± .94 | 24.37 ± .58 | 25.70 ± 1.48 |
| $TiO_2$ | .07 ± .05 | .11 ± .06 | .04 ± .02 | .06 ± .02 | .05 ± .03 | .16 ± .13 |
| $Al_2O_3$ | 33.32 ± 1.84 | 29.85 ± .87 | 31.59 ± .44 | 20.50 ± .46 | 21.46 ± .87 | 20.60 ± 1.69 |
| FeO * | 3.22 ± .97 | 6.29 ± 2.19 | 5.90 ± .55 | 43.60 ± .59 | 38.74 ± .70 | 39.11 ± 2.00 |
| MnO | .10 ± .03 | .71 ± .16 | .31 ± .07 | 2.21 ± .37 | 2.29 ± .66 | 1.28 ± .21 |
| MgO | .33 ± .24 | .50 ± .11 | .60 ± .08 | 1.26 ± .07 | 1.24 ± .21 | 3.92 ± .29 |
| CaO | ND | ND | ND | ND | ND | ND |
| $Na_2O$ | .34 ± .29 | .31 ± .13 | .30 ± .04 | ND | ND | ND |
| $K_2O$ | 10.34 ± .38 | 10.92 ± .08 | 11.03 ± .08 | .20 ± .10 | .97 ± .50 | .39 ± .30 |
| Rb (ppm) | 770 ± 200 | 1700 ± 370 | | | | |
| Ba (ppm) | 860 ± 400 | ND | | | | |

| mineral phase | BIOTITE | | | K FELDSPAR | | Na FELDSPAR | |
|---|---|---|---|---|---|---|---|
| sample | $Mo_8$ | $Mo_8$ | $Mo_{15}$ | $Mo_8$ | $Mo_{18}$ | $Mo_8$ | $Mo_{18}$ |
| $SiO_2$ | 34.68 | 36.35 | 36.03 ± .66 | 65.03 ± .38 | 65.11 ± .61 | 66.82 ± .48 | 68.00 ± .38 |
| $TiO_2$ | 1.04 | .59 | .96 ± .20 | | | | |
| $Al_2O_3$ | 18.87 | 21.06 | 21.37 ± .54 | 18.30 ± .03 | 18.64 ± .6 | 20.98 ± .37 | 20.07 ± .10 |
| FeO * | 29.54 | 25.49 | 23.08 ± .81 | | | | |
| MnO | .76 | .87 | 1.92 ± .08 | | | | |
| MgO | 3.06 | 2.72 | 1.25 ± .06 | | | | |
| CaO | ND | ND | ND | ND | ND | 1.50 ± .40 | .32 ± .20 |
| $Na_2O$ | ND | ND | ND | 1.17 ± .59 | .50 ± .40 | 10.59 ± .21 | 11.35 ± .09 |
| $K_2O$ | 6.15 | 2.44 | 9.46 ± .18 | 15.15 ± .80 | 16.17 ± .53 | .46 ± .05 | .33 ± .06 |
| Rb (ppm) | | | 2710 ± 350 | | | | |
| Ba (ppm) | | | ND | | | | |

* TOTAL IRON AS FeO

Major and trace-element abundances are expressed as weight percent and ppm, respectively. Sample identification as in tab. 1.

La and Ce are mainly associated with zircon in this rock.

Taking into account the average contents of all elements analyzed it is apparent from fig. 4 that the disseminated-$MoS_2$ bearing rocks show slightly higher contents of Na, Al, Fe, Ce and Rb than the other rocks. On the contrary, the barren rocks are comparatively somewhat enriched in K, Ti, P and Sr, while the rocks containing $MoS_2$ in quartz veins, apart from being of course enriched in $SiO_2$, show no characteristic abundances.

It is noteworthy that the disseminated-$MoS_2$ bearing leucogranites exhibit average chemical abundances that are closer for many elements, except $TiO_2$ and $P_2O_5$, to those of unaltered similar rock-types (GUASPARRI et al., 1984) than the other rocks, and in particular the barren ones. This suggests that the disseminated-$MoS_2$ bearing leucogranites were affected by weak bulk altera-

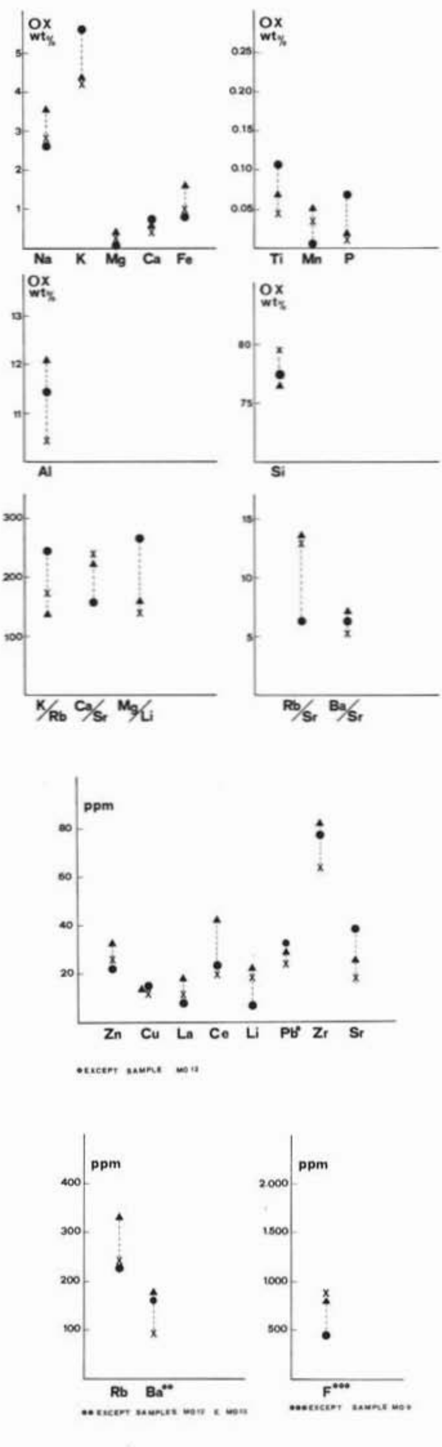



Fig. 4. — Average contents of all elements analyzed and selected interelement relationships in the wall-rocks from the Sardinian Mo showings studied. Symbols as in fig. 2.

tion, in agreement with petrographic evidence showing major alteration being restricted mainly to biotite. Weak alteration results also from fig. 5 that plots on a A-K-F diagram the Sardinian rocks and reference fields of the different alteration assemblages and fresh rock compositions of the main Mo deposits from Northern America (MUTSCHLER et al., 1981). It is in fact apparent that the Sardinian mineralized rocks cluster close to the K apex, falling within the fresh rock field. From fig. 5 it is also apparent that most barren rocks in a zone that overlaps both the fresh-rocks and argillic alteration fields, in agreement with the more pronounced alteration shown by these rocks, where plagioclase also, in addition to biotite, is sometimes altered, as suggested by the lower average Na contents of the rocks.

A weak wallrock alteration and pyritization like that of the Sardinian mineralized rocks studied is characteristic of some porphyry-type Mo deposits from Southern Finland (NURMI, 1985) and other similar occurrences of Precambrian age throughout the world (AYRES and CERNY, 1982). Another feature that is similar in both the Sardinian Mo showings and Southern Finland Mo deposits is the chemical composition of the host granitoids outside the mineralized area, that is normal with low and constant background contents of ore elements.

As concerns the interelement relationships from fig. 4 it is apparent that the mineralized (both disseminated-$MoS_2$ and quartz vein $MoS_2$-bearing) rocks show average lower K/Rb and Mg/Li ratios with respect to the barren rocks, but average higher Ca/Sr and Rb/Sr ratios and similar average Ba/Sr ratio. Therefore there is evidence that the mineralizing solutions removed from the granitoid rocks preferentially K, Mg and Sr with respect to Rb, Li and Ca respectively, while Ba and Sr were not fractionated each other. In particular the lower K/Rb ratios of the mineralized rocks with respect to those barren are consistent with the results of ARMBRUST et al. (1977), who found an increase of the Rb/K ratio toward mineralization in two Chilean porphyry copper deposits as a result of sericite alteration of the rocks. As concerns the Rb/Sr ratio, its increase from the barren rocks toward those mineralized is in agreement with the data from W-Mo-Bi deposits from Eastern Australia (PLIMER and ELLIOTT, 1979), thus confirming this ratio may be useful as a guide to mineralization in rocks that either display alteration or have no recognizable alteration.

Finally, dealing with the granodioritic rocks of the Mo showings from Ogliastra, from fig. 2 it is apparent that they do not show remarkable differences of major and selected trace-element contents relative to average unaltered granodiorite from the same area (FIORI et al., 1984), except for Cu, Zn and Zr that show higher levels in the mineralized rocks. This latter feature is in full agreement with the type of mineralization (mainly Cu and Zn sulfides) host in the Ogliastra granitoids.

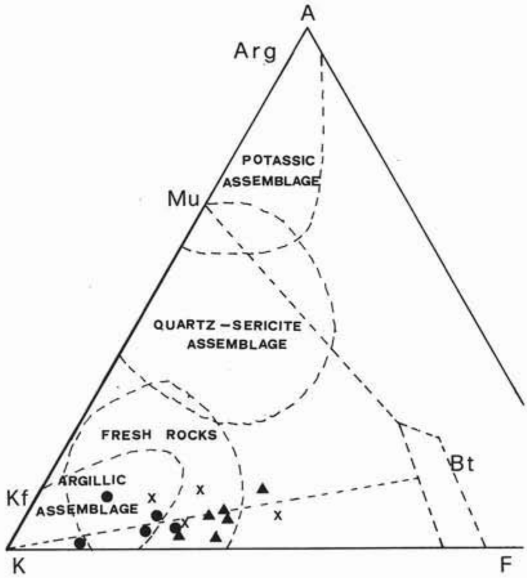



Fig. 5. — A-K-F plot for the wallrocks from the Sardinian Mo showings studied. *A* = molecular $Al_2O_3$-molecular ($Na_2O + K_2O + CaO$); *K* = molecular $K_2O$; *F* = molecular ($FeO + MgO + MnO$); *Arg* = clay minerals; *Bt* = biotite; *Kf* = potassium feldspar; *Mu* = muscovite (sericite).

## The alteration processes and ore genesis

Petrographic evidence shows, as said above, that among the four major phases of the mineralized wallrocks of the Sardinian Mo showings studied biotite is the only one affected by extensive alteration. This suggests that the altering fluids had cation/$H^+$ ratios well below permissible limits of stability of this phase. In particular alteration of biotite to chlorite, that according to CHAYES (1955) may be expressed by

$$2\,(OH)_2KFe_3AlSi_3O_{10} + 2\,H_2O \rightarrow$$

$$(OH)_8Fe_5FeAlSi_3O_{10} + KAlSi_3O_8 + K^+$$

suggests that the fluids contained high aqueous Fe relative to alkalies. Microprobe analyses of biotite of the samples studied show transformations of this phase to Fe-chlorite and K-feldspar along the cleavage lines, in full agreement with the above reaction scheme.

Release of $K^+$ from the mica lattice to the altering solutions may have increased the $K^+/H^+$ of the fluids, thus favoring sericitization of plagioclase and deposition of quartz according to the following equation (HEMLEY and JONES, 1964):

$$3\,NaAlSi_3O_8 + 2\,H^+ + K^+ =$$

$$KAl_3Si_3O_{10}(OH) + 3\,Na^+ + 6\,SiO_2\,.$$

It is in fact likely that sericitization took place during the same alteration event that caused chloritization of biotite, as sericite exhibits high (up to 7 %) contents of Fe (tab. 2), thus suggesting that it formed from solutions with relatively high Fe ion/$H^+$ ratio.

Occasional sericitization of K-feldspar, in addition to plagioclase sericitization, may have occurred due to decrease of aqueous $SiO_2$ activity because of precipitation of quartz, as indicated by the following equation that is shifted to the right (HEMLEY and JONES, 1964):

$$1.5\,KAlSi_3O_8 + H^+ =$$

$$0.5\,KAl_3Si_3O_{10}(OH)_2 + K^+ + 3\,SiO_2\,.$$

Sericitization of K-feldspar may also have been favored by either a decrease of temperature or in the alkali ion/$H^+$ ratio at constant pressure.

The presence of sericite and quartz of new formation in the mineralized rocks studied allows to define some of the physicochemical characteristics of the altering-mineralizing fluids. In particular deposition of quartz from the hydrothermal fluids suggests that activity of aqueous silica was close to the values for quartz saturation and pH of the solutions was low, as crystalline silica is soluble in alkaline solutions. Occurrence of well-shaped sericite in all the rocks studied fully supports this latter suggestion, as this phase is stable in acidic solutions. Moreover, comparison of the chemical compositions of sericite from the three major deposits shows that there is a close resemblance of contents for many elements, major differences being restricted to Mn and perhaps Rb and Ba (tab. 2). This suggests that, despite these deposits are far from each other (fig. 1), sericite was deposited under rather similar physico-chemical conditions, in particular from fluids of close chemistry. This is in agreement with the hypothesis saying the Sardinian Mo showings formed from liquids linked to the emplacement of leucogranitic magmas during the late stage of the Hercynian orogenesis (GUASPARRI et al., 1984). Finally, as indicated from tab. 2 sericite from Perda Majori deposit exhibits lower Rb/K ratios than the associated magmatic biotite. This may be accounted for by the lower temperature of deposition of sericite relative to biotite, in agreement with BESWICH (1973), who found an increasing partitioning of Rb relative to K into the vapor phase with decreasing temperature with respect to phlogopite, assuming that, as seems reasonable, a similar relationship holds for sericite.

However, as indicated by chemistry of most of the mineralized rocks studied, both K-feldspar and the bulk plagioclase were scarcely altered to sericite, thus indicating that the alkali ion/$H^+$ ratios of the altering solutions were high enough to keep the bulk of both feldspar stable (HEMLEY and JONES, 1964). In particular, because stability of plagioclase requires higher alkali chloride/HCl ratios in the solutions than that of K-feldspar, assuming that the Na/K ratios of the solutions were equilibrated with both feldspars at about 400° C ([1]), it is calculated that aqueous mNaCl/mKCl was approximately 5 for the coexistence of plagioclase and K-feldspar (ORVILLE, 1963).

The higher degree of alteration of plagioclase in the barren rocks with respect to those mineralized suggests lower NaCl/HCl ratios in the fluids that altered the former rocks. Therefore, if the altering fluids of both mineralized and barren rocks were to some extent related within a same genetic framework, there is suggestion that these fluids were progressively lesser saline moving outward from the mineralized zone. Alternatively it is possible that the alteration of the barren rocks was mainly due to weathering, thus indicating the mineralizating processes were restricted to very small portions of the granitoid rocks, as the barren sample were collected within short (less than 100 m) distance from the ore occurrence.

The chemical features of the mineralized wallrocks studied do not allow to assign the altering fluids a definite origin, but as in many other ore deposits connected with magmatism it is likely that the fluids were a mixture of both magmatic solutions and meteoric waters (e.g. SHEPPARD et al., 1971). In this view, as the Sardinian leucogranites were emplaced at shallow depth in the crust, probably lesser than 4 km (GUASPARRI et al., 1984), then it is likely that these shallow intrusions started hydrothermal circulation systems that caused wallrock alteration. However alteration was mainly restricted to the granitic bodies themselves, and only to lower extent affected the metamorphic cover, as indicated by field evidence (GUASPARRI et al., 1984) and suggested by the low Mg and high Fe contents of chlorite in the rocks studied (tab. 2) indicating leaching and circulation of the fluids mainly through acidic rocks. Therefore it is possible to put some constraints to the provenance of base metals of the mineralization, and in particular of Mo. The bulk of this latter thus could not derive from leaching of the metamorphic rocks intruded by the granitic magmas, but likely from these latter. In this view, as Mo is an element incompatible with major igneous rock-forming minerals and tends to be concentrated in the residual liquid and vapor phases of any magmatic system (KRAUPSKOPF, 1979), then

([1]) If alteration temperatures were low, kaolinite would probably have formed instead of sericite (HEMLEY and JONES, 1964).

it seems reasonable that the bulk of Mo was carried by the late magmatic fluids.

These latter are expected to be rich in K and depleted in $Al_2O_3$, as suggested by the close relation between Mo and K observed in several deposits (WESTRA and KEITH, 1981). The magmatic fluids merging into the meteoric waters introduced Mo in the hydrothermal system, where Mo is largely transported as $HMoO_4^-$ with lesser amounts contained in $H_2MoO_4$ and $MoO_3F^-$ (SMITH et al., 1980).

In such systems Mo concentration may reach several thousand part per million at 350° C, but its solubility decreases drastically between 350° and 300° C.

The low grade of the Sardinian Mo showings may reflect either the slight grade of geochemical specialization of the leucogranites (BISTE, 1982) and/or some unfavorable geologic conditions (GUASPARRI et al., 1984). With respect to the first hypothesis it is noticed that according to MUTSCHLER et al. (1981) a F content $\geqslant 0.1$ percent is diagnostic of granite-molybdenite systems. F is important as high F contents in the magmas increase the solidus temperature and favor crystallization, decreasing the water solubility in the magmas. This, in turn, increases the possibility of forming hydrous K-rich silicate melts than can concentrate Mo. Therefore, with respect to F content of the Sardinian rocks analyzed, it is apparent that only in a few samples it is greater than 0.1 %, this possibly accounting for the low grade of the Mo mineralization. The low grade of the Mo mineralization perhaps depends also on the low grade of hydrothermal alteration, well evidenced by the scarce amount of newly-formed K silicates in the rocks studied.

Finally the absence of major propylitic halo that is typical of many Mo deposits throughout the world (e.g. WESTRA and KEITH, 1981) may be explained by the fact that leaching of the leucogranites could not provide large amounts of Ca, Mg, and Fe to the mineralizing solutions to be deposited in the form of calcite and epidote in the outer zones of the mineralization. Propylitic alteration is, on the contrary, more developed in the Ogliastra showings, in agreement with the more mafic character of the wallrocks. These latter likely provided most of Cu and Zn, that represent the main base metals of the Ogliastra mineralization, where $MoS_2$ if of subordinate importance.

## Appendix

### BRIEF DESCRIPTION OF THE MAIN CHARACTERISTICS OF THE SARDINIAN MO SHOWINGS STUDIED

*Locality*: MONTE CORILLA
*Rock-type*: leucogranite.
*Wallrock alteration*: plagioclase to sericite and rarely to epidote; scarce sericite upon K-feldspar; several veinlets of calcite through the rocks.
*Ore occurrence*: both disseminated and quartz veinlet stockwork.
*Ore paragenesis*: molybdenite with subordinate sphalerite, galena, chalcopyrite and rare wolframite; abundant pyrite in veinlets; Fe oxides.

*Locality*: SU SEINARGIU
*Rock-type*: porphyritic leucogranite.
*Wallrock alteration*: plagioclase to sericite and clay minerals.
*Ore occurrence*: both disseminated and quartz veinlet stockwork.
*Ore paragenesis*: molybdenite and pyrite with subordinate chalcopyrite and rare wolframite.

*Locality*: PERDA E PIBERA
*Rock-type*: medium-grained leucogranite.
*Wallrock alteration*: plagioclase to sericite and clay minerals; biotite to chlorite or sometimes to sericite and calcite.
*Ore occurrence*: both disseminated and quartz veinlet stockwork.
*Ore paragenesis*: molybdenite with subordinate sphalerite, galena and pyrite.

*Locality*: PERDA MAJORI
*Rock-type*: leucogranite.
*Wallrock alteration*: plagioclase to sericite and clay minerals, biotite to chlorite and sometimes to sericite, K-feldspar rarely to sericite.
*Ore occurrence*: quartz veinlet, stockwork.
*Ore paragenesis*: molybdenite, wolframite and pyrite with subordinate chalcopyrite, sphalerite, galena and bismuthinite, topaz.

*Locality*: SERRA MANDRA and GOENE
*Rock-type*: biotite granodiorite.
*Wallrock alteration*: plagioclase to sericite, biotite to chlorite and sometimes to epidote.
*Ore occurrence*: disseminated.
*Ore paragenesis*: sphalerite with blebs of chalcopyrite, chalcopyrite, molybdenite, galena and magnetite.

*Locality*: BADDE SA FIGU
*Rock-type*: fine-grained leucogranite.
*Wallrock alteration*: biotite to chlorite and rarely to sericite, plagioclase to sericite and clay minerals; K-feldspar sometimes to sericite.
*Ore occurrence*: disseminated.
*Ore paragenesis*: molybdenite and pyrite; fluorite.

*Locality*: S'ABBAGANA
*Rock-type*: fine-grained leucogranite.
*Wallrock alteration*: plagioclase to sericite and clay minerals, biotite to chlorite and sericite, K-feldspar sometimes to sericite.
*Ore occurrence*: both disseminated and quartz veinlet stockwork.
*Ore paragenesis*: molybdenite and pyrite.

*Locality*: MONTE MANNU
*Rock-type*: coarse- to medium-grained leucogranite.
*Wallrock alteration*: plagioclase to sericite, and sometimes to calcite, biotite to chlorite and sericite, K-feldspar sometimes to sericite.
*Ore occurrence*: disseminated.
*Ore paragenesis*: molybdenite, pyrite with subordinate chalcopyrite and wolframite.

*Acknowledgements.* — This work has been carried out with the financial aid of C.N.R., Centro Studi Geominerari e Mineralurgici, c/o Istituto di Giacimenti Minerari, Geofisica e Scienze Geologiche, Facoltà di Ingegneria, Università di Cagliari.

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